

## Laboratory, Observational and Theoretical Studies of Interstellar Ices.

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### 1. - Introduction.

The application of spectroscopic studies of gaseous species (atoms, ions and molecules) to the interpretation of astronomical spectra dates back to the previous century. The parallel approach to the study of interstellar dust is, however, rather recent. Although the existence of interstellar dust was recognized in the 1930's [1], laboratory studies of dust analogs have begun only recently, with the first serious attempts in the 1960's [2]. Even with this, the effort devoted to dust has been much less than that devoted to the gas phase. This situation has recently changed due to the development of sophisticated ground-, air- and space-based observational techniques, especially in the infrared. To fully exploit these new observations it has become necessary to study laboratory analogs.

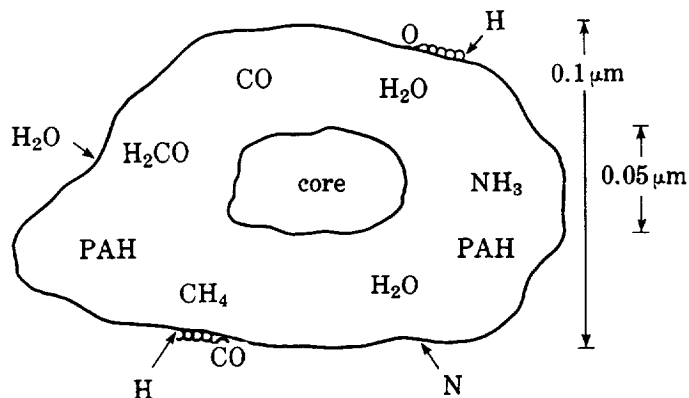
One of the most active areas of laboratory work has been the study of the properties of various mixed ices of astrophysical interest. For example, particle bombardment experiments on ice samples have been made to investigate the effects of sputtering and ion chemistry by solar wind and cosmic-ray irradiation [3-7]. Similar studies have been made using ultraviolet photons instead of ions [8-11]. Many of these studies utilized spectroscopic techniques to analyze the results. General reviews of this emerging field have appeared over the last decade [2, 12, 13]. Some references which contain detailed quantitative spectroscopic information on astrophysically relevant ices are [14-19]. While not exhaustive, the references listed above and references therein provide a good overview of the work in this field.

This lecture presents an overview of our current understanding of interstellar ices. It borrows heavily from several reviews that we have published previously [12, 13, 20-22]. In sect. 2 the chemistry of interstellar icy grain mantles is discussed. Besides a review of theoretical calculations of grain

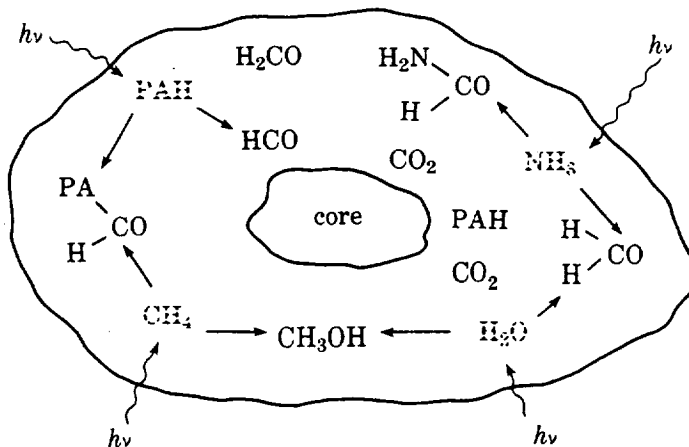
surface chemistry occurring upon accretion, it also summarizes the results of various laboratory experiments on the effects of UV irradiation on ices. After a brief description of the basic laboratory techniques involved in (interstellar) ice analog studies (sect. 3), the fundamentals of infrared spectroscopy are reviewed (sect. 4) with an emphasis on solid-state effects. This is then illustrated with an analysis of the spectrum of  $\text{H}_2\text{O}$  ice and a quantitative description of column density determinations. The observed composition of interstellar ices derived from IR observations of protostars embedded inside dense clouds is then discussed and compared to the results of theoretical calculations (sect. 5). Finally, sect. 6 presents a summary of this lecture.

grain mantle growth and evolution

grain surface reactions produce simple molecules



UV irradiation produces complex molecules



without some form of energetic processing, mantles  
will be made up primarily of simple molecules

Fig. 1. - Representation of the types of core-mantle grains expected in molecular clouds.

## 2. – Icy grain mantles in dense molecular clouds.

Dense interstellar clouds are comprised of gas and dust. The gas is a mixture of many different atomic and molecular species. During the past three decades radio astronomers have discovered more than fifty interstellar polyatomic molecules in these clouds[23]. Interspersed with the gas, at much lower abundance ( $\approx 10^{-12}$  per H atom), are small ( $\approx 1000 \text{ \AA}$ ), cold ( $\approx 10 \text{ K}$ ) dust particles. Because the grains are cold, most gaseous species (except H, He and  $\text{H}_2$ ) striking the grains will stick, forming a mixed molecular ice mantle. The accreting atoms, radicals and molecules may react with each other. At this point in our understanding of chemistry in clouds, two general classes of molecular mantle are envisioned. One class is comprised largely of relatively simple species formed by grain surface reactions. The other consists of a chemically more complex mixture resulting from UV photolysis of this simple mixture (fig. 1). These are often called «icy» grain mantles and organic refractory grain mantles, respectively, in the literature. They will be discussed in turn in the remainder of this section.

*2.1. Grain surface chemistry.* – Gas phase species colliding with cold ( $\approx 10 \text{ K}$ ), interstellar grains are expected to stick to the surface with almost unit probability[20]. Although the flux of incoming species is typically very low (few/day), all heavy-gas phase species should have accreted in about  $10^5 \text{ y}$  at a density of  $10^4 \text{ cm}^{-3}$ . Since some of the accreted species will be mobile (*i.e.* atomic H and O) on such surfaces, reactions between them, as well as with immobile species, are important and will lead to the formation of a molecular grain mantle whose composition may be quite different from the gas phase[24-27]. This is illustrated in fig. 2 which compares the calculated gas phase and grain mantle composition of interstellar clouds as a function of total gas phase density.

In the gas phase, hydrogen is mainly in the form of  $\text{H}_2$ , carbon in the form of CO, nitrogen and the remainder of the oxygen are either in atomic (N, O) or diatomic ( $\text{N}_2$ ,  $\text{O}_2$ ) form, depending on the physical conditions (fig. 2). At low densities atomic H is an important constituent of the gas phase and it dominates the grain surface reactions. Under such reducing conditions, hydrides such as  $\text{H}_2\text{O}$  and  $\text{H}_2\text{CO}$  formed from O,  $\text{O}_2$  and CO are calculated to be abundant grain mantle species (fig. 2). Note that the grain mantle abundance of  $\text{NH}_3$  is low since most of the elemental N in the gas phase is in the form of  $\text{N}_2$  and its reaction with H is inhibited by a large activation barrier. Likewise, little  $\text{CH}_4$  is formed since most of the elemental C is in the form of CO. In these calculations, reduction of CO was stopped at  $\text{H}_2\text{CO}$ . Recent laboratory experiments suggest that the H addition to  $\text{H}_2\text{CO}$  has a low activation energy[28] and most of the  $\text{H}_2\text{CO}$  in the grain mantles might actually be reduced to  $\text{CH}_3\text{OH}$ .

At high densities, the gas phase abundance of heavy species is much larger

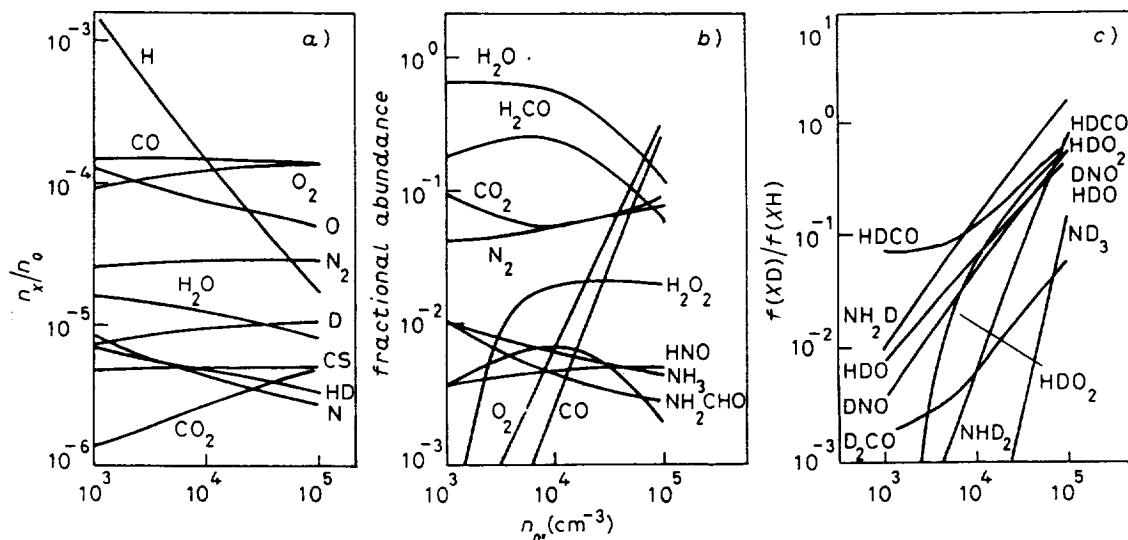


Fig. 2. – A comparison of the calculated gas phase and solid-state composition of a molecular cloud: a) gas phase, b) grain mantle, c) deuteration. When atomic H dominates over heavy species in the gas phase, accreting species will be hydrogenated. Otherwise grain mantles will reflect the gas phase more directly. Note that large deuterium enrichments are expected to be a characteristic of grain mantles as a result of the high atomic D/H ratio in the gas phase (adapted from ref. [24, 25]).

than that of atomic H and as a result the composition of the grain mantle will be quite different. When atomic O has a low gas phase abundance, few grain surface reactions will occur and an inert grain mantle will result, consisting mainly of CO and  $\text{O}_2$  (fig. 2), which reflects their gas phase dominance. However, if the gas phase O abundance is high, CO may be oxidized to  $\text{CO}_2$ . It has been suggested that this reaction is inhibited at low temperatures by an activation barrier [29]. However, while O atoms can be stored in a CO matrix at 10 K,  $\text{CO}_2$  is formed immediately when the matrix is warmed [30]. The reaction seems, therefore, to be mainly inhibited by steric factors rather than by an activation barrier. Steric factors are probably less important on a grain surface than in a matrix and  $\text{CO}_2$  might be an important grain mantle constituent under these conditions. Further experimental studies are important to better determine the kinetics of this reaction at low temperatures.

Grain surface reactions can also lead to large deuteration effects (fig. 2[25, 27]). The D and H grain surface reaction networks are very similar and this deuteration directly reflects the high gas phase D to H ratio ( $> 10^{-2}$ ), which is much larger than the elemental abundance ratio ( $\approx 10^{-5}$ ). This is a direct consequence of ion-molecule gas phase chemistry which produces high abundances of deuterated ions (*i.e.*  $\text{DCO}^+$ ), that dissociatively recombine with electrons to form atomic D [25, 31].

In summary, theoretical calculations predict that grain surface chemistry

can produce three different components of icy grain mantles in molecular clouds depending on the physical conditions in the gas phase. They are 1) a reduced component (*i.e.*  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ ), 2) an inert component (*i.e.*  $\text{CO}$  and  $\text{O}_2$ ) and 3) an oxidized component (*i.e.*  $\text{CO}_2$ ). Although in any given region one component will be dominant, along a line of sight multiple components may be present. Another characteristic of grain surface reactions is large deuterium fractionation of hydrides.

**2.2. UV photolysis of icy grain mantles.** – Significantly more complex ice mantles should be produced by energetic processing with ultraviolet radiation and cosmic rays [3, 32]. The products of irradiation span a broad range in complexity, starting with molecules as «simple» as  $\text{CO}_2$  and  $\text{H}_2\text{CO}$ , and extending to large, poorly characterized «polymers» [20]. UV photolysis of simple molecular ices produces reactive radicals (such as  $\text{H}$ ,  $\text{O}$  and  $\text{OH}$ ), often in electronic or vibrationally excited states. These radicals can react with their neighbors or diffuse through the ice and react with other species present. Because of the large amount of excess energy available, even reactions with molecules having closed electronic shells, which normally have appreciable activation barriers, become possible. An example of the possible reaction pathways involving  $\text{CO}$  and the simple photoproducts of an ice made of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{NH}_3$  is shown in fig. 3. Note how even a few steps are sufficient to produce complex molecules, such as acetaldehyde ( $\text{CH}_3\text{CHO}$ ).

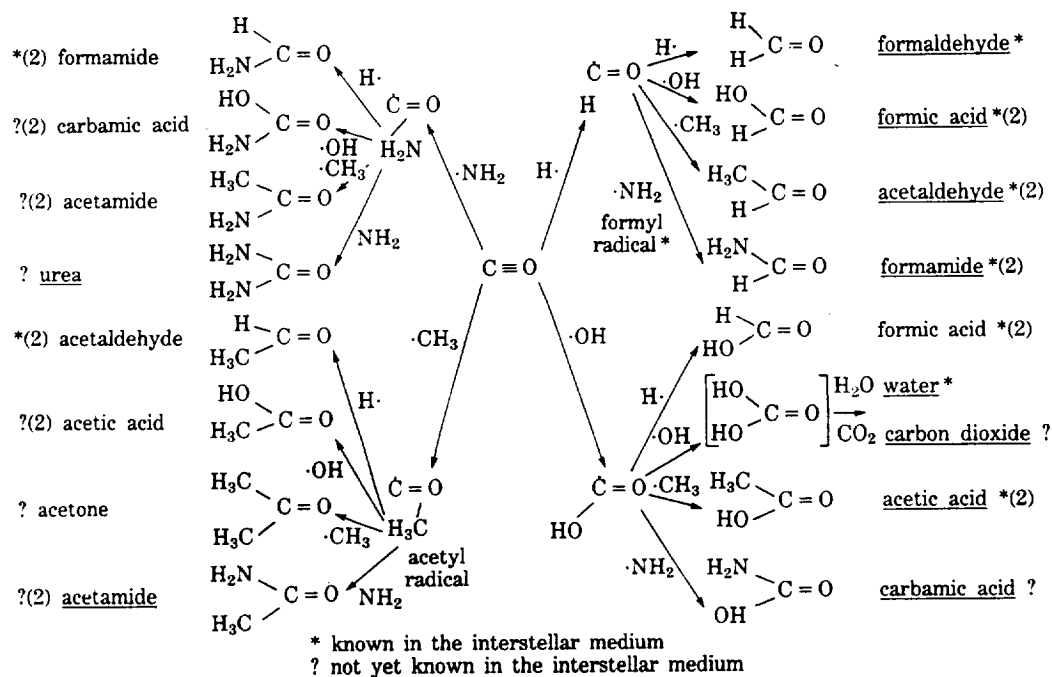


Fig. 3. – Possible reaction pathways involving  $\text{CO}$  in an interstellar grain mantle illustrating how the intermediates  $\text{H}$ ,  $\text{OH}$ ,  $\text{CH}_3$  and  $\text{NH}_2$  can add to  $\text{CO}$  and produce a very rich chemical mixture.

Since the diffusing radicals may lose most of their excess energy through collisions with matrix molecules before finding a reaction partner, they can also be stored at low temperatures in interstitial or substitutional sites. Upon warm-up above 30 K these radicals can diffuse again and react, forming more complex molecules and resulting in a so-called organic refractory grain mantle [9, 32-34]. Whether this actually takes place inside dense interstellar clouds depends on two conditions: 1) The presence of an internal UV source and 2) the presence of a (transient) heating mechanism for grain mantles [20]. Cosmic rays may play a major role for both conditions. Cosmic-ray excitation of  $\text{H}_2$  molecules leads to UV fluorescence in the Lyman-Werner bands, resulting in an average UV field in the cloud of about  $10^3 \text{ photons cm}^{-2} \text{ s}^{-1}$  [35, 36]. This is sufficient to produce a stored radical concentration of about 1% in a grain mantle in about  $2 \cdot 10^4 \text{ y}$ . A larger concentration of radicals is inhibited by recombination of «hot», diffusing radicals with stored radicals. However, transient heating of grain mantles by cosmic rays to about 30 K occurs at a similar time scale [37] and will lead to diffusion and reaction of these stored radicals. The process can then start over again. Grain-grain collisions with relative velocities in excess of 50 m/s will also produce warming above 30 K and can trigger the diffusion and reaction of stored radicals [33].

Extensive laboratory studies have been done on UV photolysis and warm-up of molecular ices containing  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}$  and  $\text{CH}_4$  at various concentrations [9, 11, 34]. Besides the original matrix molecules, many simple newly formed molecules (*i.e.*  $\text{HCOOH}$ ,  $\text{HCONH}_2$ ,  $\text{CO}_2$ ,  $\text{HCO}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HNO}$ ) are released upon warm-up. After warm-up above 150 K most of the deposited matrix molecules (*i.e.*  $\text{H}_2\text{O}$ ) have evaporated and a refractory residue with an enhanced C abundance is left behind. The composition of some of these residues has been determined by gas chromatography/mass

TABLE I. – *The composition of an organic residue(\*)*.

Species	Formula	Abundance
glycolic acid	$\text{HOCH}_2\text{COOH}$	0.38
hydroxyacetamide	$\text{HOCH}_2\text{CONH}_2$	0.13
oxamic acid	$\text{H}_2\text{NCOCOOH}$	0.05
glycerol	$\text{HOCH}_2\text{CHOHCH}_2\text{OH}$	0.06
oxamide	$\text{H}_2\text{NCOCONH}_2$	0.15
glyceric acid	$\text{HOCH}_2\text{CHOHCOOH}$	0.07
glyceramide	$\text{HOCH}_2\text{CHOHCONH}_2$	0.16

(\*) Initial mixture  $\text{H}_2\text{O}/\text{CO}/\text{CH}_4/\text{N H}_3 = 10/3/3/1$ .

spectrometer analysis (table I [34]). Similar molecules are produced by energetic ion bombardment of such ices [38]. Typically, these residues consist of small organic molecules with OH, C=O, NH<sub>2</sub> and CH<sub>2</sub> groups and contain 5 to 7 heavy elements of which 2 to 3 are C atoms (smaller molecules generally evaporate below room temperature). Essentially, these molecules are formed by the addition of a few simple building blocks, such as OH, NH<sub>2</sub> and HCO. By adding a few steps to the scheme shown in fig. 3, plausible reaction networks for their chemical formation can be made [34]. In view of the limited number of building blocks, pronounced chemical selectivity will result. In particular, the residues studied are dominated by carboxylic acids, alcohols and amides, which merely reflects the dominance of saturated hydrides and CO in the initial mixture. Although a different initial mixture may result in a different chemical composition of the residue, we can conclude in general that UV photolysis of icy grain mantles will be chemically specific.

Finally, prolonged exposure to UV photons may eventually lead to the loss of most of the elements other than C. Indeed, there is some laboratory evidence for the formation of unsaturated carbon bonds upon prolonged photolysis. Eventually, such processing may actually lead to an amorphous carbon network, consisting of aromatic units linked by aliphatic chains, similar to that resulting from pyrolysis of terrestrial kerogen. A rough estimate for the time scale involved for this process in the diffuse interstellar medium is about 1 My. Inside dense clouds the UV photon density is too low for this to be of importance. Whether this process is of importance on a galactic scale depends then on the ratio of this conversion time scale to the shock destruction time scale for the organic residue in the diffuse interstellar medium. It is quite conceivable that the latter is relatively long (> 10 My) and that amorphous carbon—a grain component normally assumed to result from processes around red giants—is also formed in the ISM.

### 3. – Interstellar ice analog production.

Mid-infrared absorption spectroscopy of dense interstellar clouds generally depends on the presence of embedded or background infrared continuum sources. Figure 4 illustrates the geometry typical of interstellar absorption objects. Radiation from the source heats the immediately surrounding dust. This hot dust emits an infrared pseudoblackbody continuum like that shown in the inset close to the protostar in fig. 4. As this radiation passes through the cloud, molecules along the line of sight absorb at their fundamental frequencies resulting in a spectrum which shows absorption features diagnostic of the material (lower inset in fig. 4). Ice features generally dominate this type of absorption spectra. The key features of interstellar-cloud environments

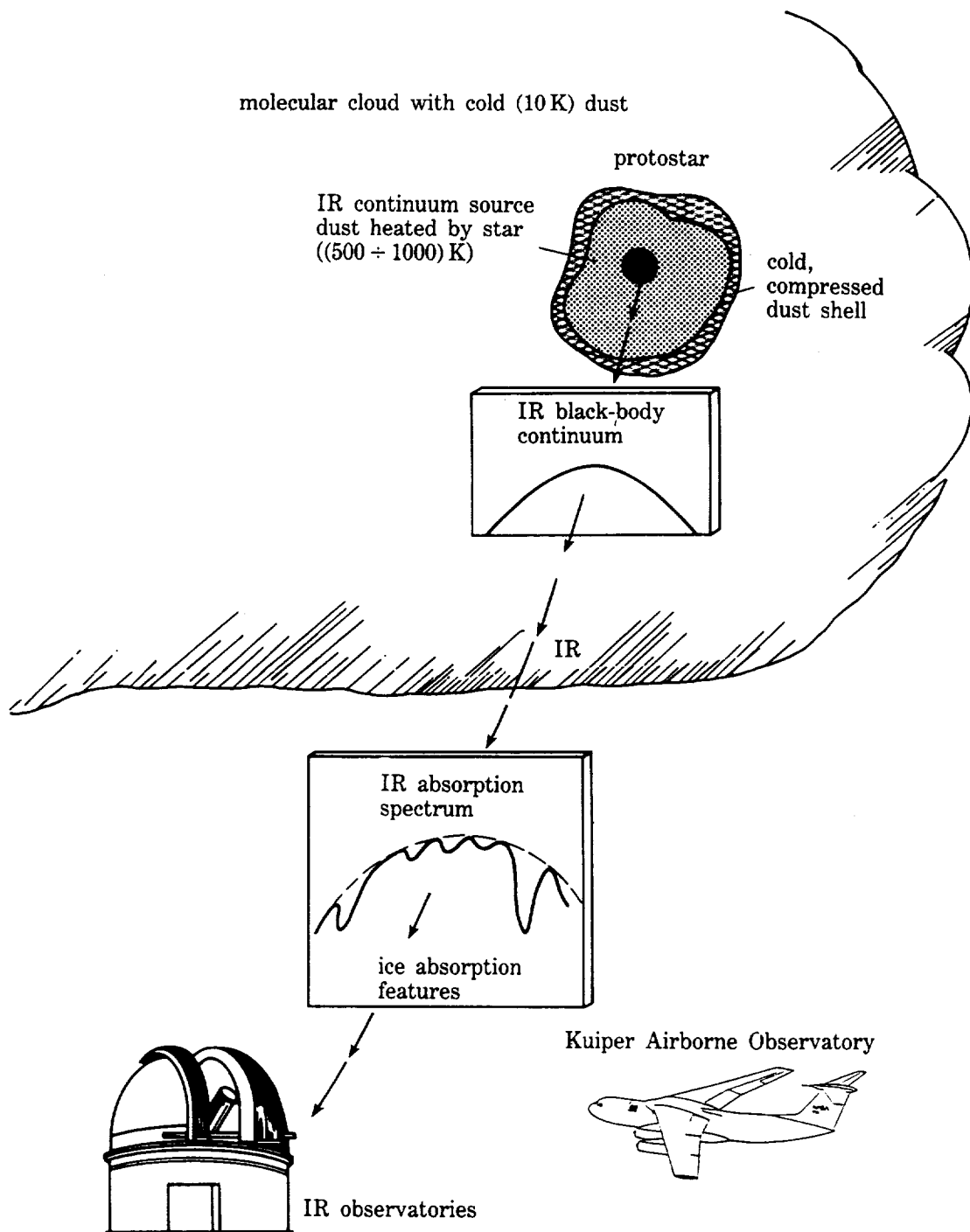


Fig. 4. – Schematic of how one obtains absorption spectra of interstellar ices.

shown in fig. 4 (infrared source, absorbing material and detection) must be mimicked in laboratory studies of ice analogs.

The spectroscopic study of low-temperature solids was developed in the first



part of this century. Of particular significance is the matrix isolation approach developed by PIMENTEL and colleagues[39]. The various sample preparation techniques which have evolved over the years, and several theoretical treatments of the interactions in the solid state can be found in various reviews[40-42]. The study of interstellar and cometary ice analogs is based on this foundation.

Since the experimental procedures used to study interstellar and cometary ice analogs have been presented in detail elsewhere[8], the method will only be summarized here. The specific conditions which must be duplicated to create interstellar ice analogs vary widely. Composition, temperature and exposure to radiation are all parameters that can be duplicated and varied in the laboratory. The general procedure consists of slowly flowing the gas from which the ice is made into a high-vacuum chamber. This gas, which can be a pure substance or a mixture of pure substances, is directed to and condenses on the surface of a substrate cooled by a closed-cycle helium refrigerator or by a cryogen such as

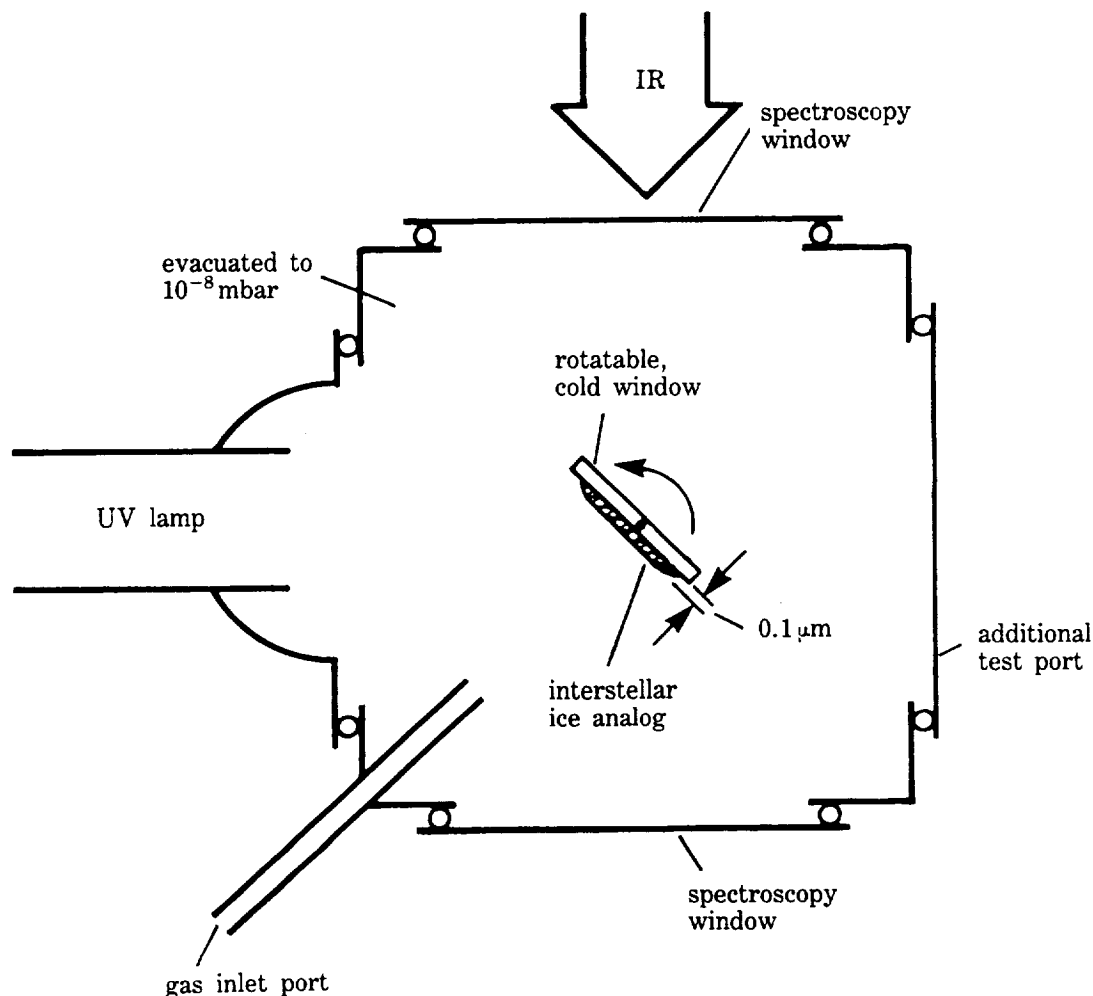


Fig. 5. - Schematic representation of the interstellar and cometary ice analog sample chamber at NASA Ames Research Center.

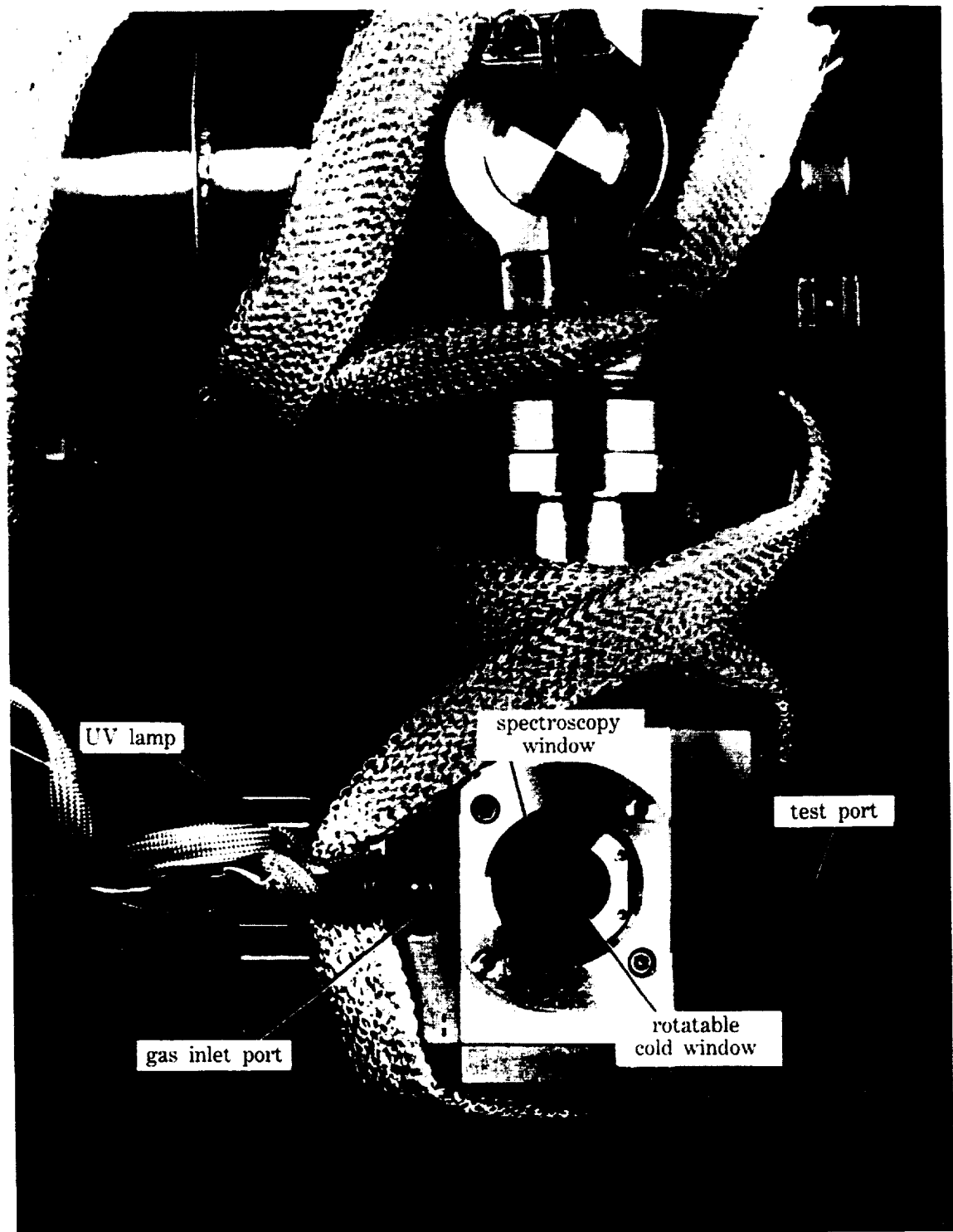


Fig. 6. - Photograph of an ice analog sample chamber at NASA Ames Research Center. The base is approximately 10 cm on a side and the cold window is about 2 cm in diameter.

liquid helium. A schematic drawing of a typical sample chamber is shown in fig. 5 and a photograph of the apparatus at Ames is given in fig. 6. Substrate temperature can generally be maintained anywhere from 10 K to room temperature. The substrate is interchangeable. For infrared studies it is generally a salt (*e.g.*, CsI) window. The substrate is rotatable and is suspended in the center of a sample chamber with gas inlet tubes and several larger ports. The larger openings can be fitted with windows, lamps, ion sources, ovens, pressure gauges, mass spectrometers, phototubes, etc., depending upon the particular ice properties under study. Generally, the substrate is initially positioned to face the gas inlet tube for the preparation of the ice and then rotated to face the other ports as needed. Radiation processing of the sample can be carried out with ultraviolet lamps or ion sources. Photoprocessing of the sample with vacuum ultraviolet radiation is carried out with a microwave powered hydrogen discharge lamp. This has a sharp Lyman  $\alpha$  peak at 121.6 nm and a 50 nm broad component centered at roughly 160 nm. Subsequently, the evaporation characteristics of the ice can be studied by measuring spectra during warm-up of the substrate.

The infrared spectrum is measured and plotted as  $\log[I_0(\nu)/I(\nu)]$  vs. frequency, where  $I_0(\nu)$  is the single-beam spectrum measured through the substrate before sample deposition and  $I(\nu)$  the spectrum measured after. When optical constants ( $n$  and  $k$ ) or integrated absorbance values ( $A$ ) are to be determined, the infrared transmission spectrum through a sample of known thickness must be measured. Sample thickness is measured by monitoring the temporal development of the thin-film interference pattern of a He-Ne laser beam reflected off or transmitted through the sample during deposition. For a description of the technique and its application to astrophysics as well as a discussion of how to derive  $n$  and  $k$  values or  $A$  values, see ref. [14, 18].

#### 4. – Infrared spectroscopy.

The infrared spectrum of a compound gives a great deal of information about that compound's structure. This is because molecular transitions which fall in this spectral region occur at the molecule's characteristic vibrational frequencies. While the infrared spectrum is characteristic of the entire molecule, certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic group frequencies that make IR spectroscopy such a powerful probe of the composition of interstellar dust and gas. For a thorough description of infrared molecular spectroscopy, the reader is referred to [43], or for a more introductory level to [44]. In this section the effects the solid state has on the infrared spectra of molecules will be reviewed in order to analyze the infrared properties of interstellar dust.

4.1. *Vibration-rotation spectroscopy.* – The frequencies of molecular vibrations are determined by the masses of the vibrating atoms, the molecular geometry and the forces holding the atoms in their equilibrium positions. To a first approximation, the vibrations of a diatomic molecule can be represented as a quantum-mechanical harmonic oscillator with the fundamental vibrational frequency,  $\nu$ , given by

$$(1) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},$$

where  $k$  is the chemical bond force constant and  $\mu$  the reduced mass ( $m_1 m_2 / (m_1 + m_2)$ ), where  $m_1$  and  $m_2$  are the masses of atoms 1 and 2. This formalism can also be used to approximate the stretching frequencies of polyatomic molecules. The combination of the masses of the most cosmically abundant atoms, H, O, C and N, with the kinds of chemical bonds they form restricts most of the fundamental vibrational frequencies for virtually all molecules made up of these atoms to the 4000 to 500  $\text{cm}^{-1}$  ( $2.5 \div 20 \mu\text{m}$ ) region. However, only those modes for which a dipole moment changes during the vibration will give rise to absorption or emission of infrared photons. Thus the vibrations of all homonuclear diatomic molecules (*e.g.*,  $\text{O}_2$ ,  $\text{N}_2$ , ...), as well as the centrosymmetric vibrations of symmetric molecules, are inaccessible to the infrared spectroscopist.

In general, since certain groups of atoms consistently absorb at or near the same frequency regardless of the rest of the molecule, virtually all molecules containing these groups possess a characteristic vibrational absorption spectrum [45, 46]. The reason for this, in rather oversimplified language, is that chemical bonds generally fall into three distinct types which are classified as single, double and triple bonds, depending upon the number of electrons participating in the bond. The term single bond is used to represent a bond in which a total of two electrons occupy the bonding molecular orbital, the double bond has four and the triple bond six. The more bonding electrons, the stronger the force constant and, as implicit in eq. (1), the higher the vibrational frequency. Conversely, keeping the type of bond constant but increasing the masses of the vibrating atoms results in a reduction of the fundamental vibrational frequency. This is illustrated in fig. 7, where the characteristic frequencies of various groups are schematically represented. The stretching vibration of the single bonds C-H, O-H and N-H all occur near 3000  $\text{cm}^{-1}$ , whereas the single bonded C-O, C-N or C-C stretches lie in a lower frequency range centered at about 1000  $\text{cm}^{-1}$ . Inspection of fig. 7 also shows that increasing the bond strength from a singly bonded carbon through doubly bonded to triply bonded carbon implies an increase of the stretching frequency from 1000  $\text{cm}^{-1}$  to above 2000  $\text{cm}^{-1}$ . As fig. 7 clearly demonstrates, absorption in

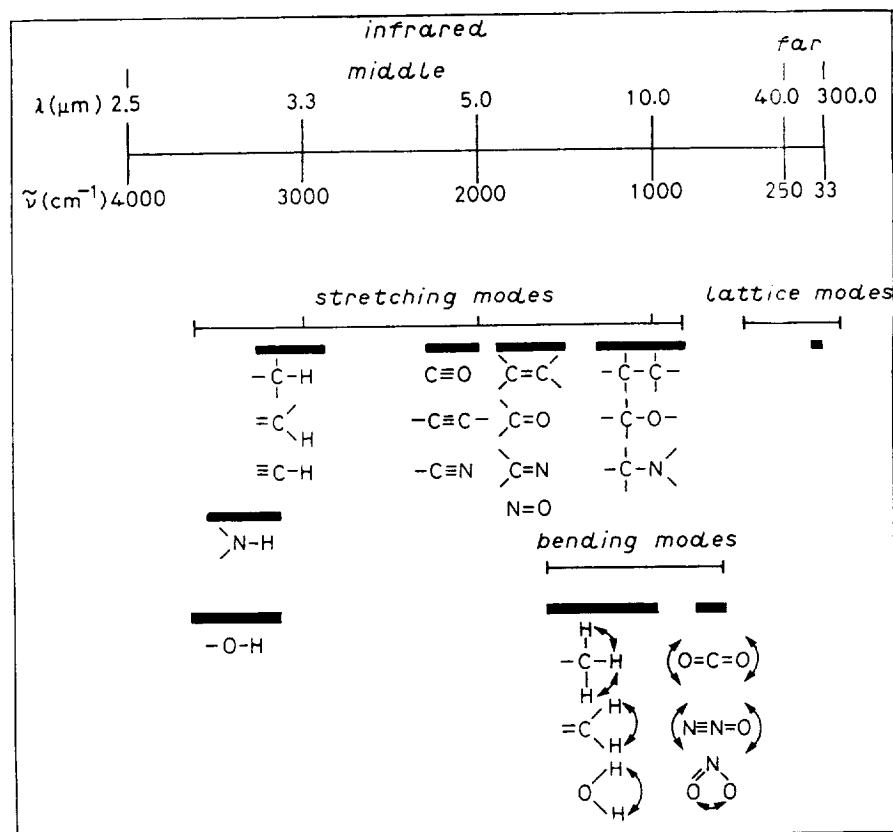


Fig. 7. - Vibrational-frequency ranges of various molecular groups.

each of these specific regions can be used to deduce the type of molecules which are present.

4.2. *Solid-state effects.* - Figure 8 shows that there are dramatic differences between the infrared spectrum of a gas phase sample and for the same sample in the solid phase. These differences are due to the following three solid-state effects: 1) rotational-structure suppression, 2) line broadening and 3) line shifting. Each will be discussed in turn.

4.2.1. - *Rotational-structure suppression.* In interstellar clouds, molecules are in both the gaseous and solid phases. In addition to undergoing internal vibrations, molecules in the gas phase can rotate. Since the energies involved in rotational transitions correspond to frequencies of only a few wave numbers, and selection rules allow rotational transitions to occur simultaneously with vibrational transitions, rotational structure is superimposed on the vibrational transitions. This gives rise to vibration-rotation bands. In the case of symmetric, polyatomic molecules the lines making up a rotation-vibration band produce a recognizable pattern which resembles the rotational-level population distribution. The transitions involving an increase in the rotational quantum

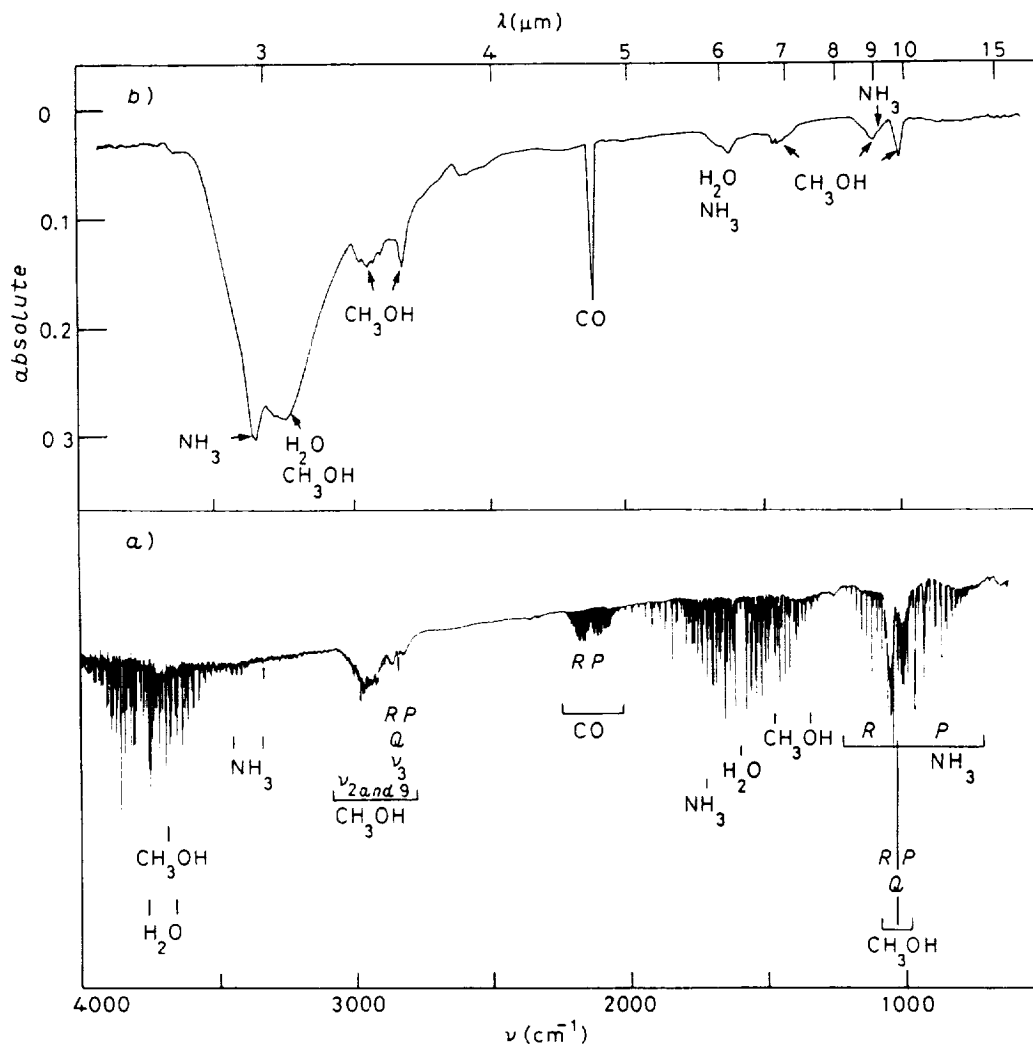


Fig. 8. - A comparison between the infrared spectrum of the mixture  $\text{H}_2\text{O}:\text{CO}:\text{CH}_3\text{OH}:\text{NH}_3$  (6:3:3:2) a) in the gas phase at room temperature and 14 mbar and b) as an amorphous solid at 10 K. Both spectra taken at  $1\text{ cm}^{-1}$  resolution.

number  $J$  give rise to the so-called  $R$  branch, those corresponding to a decrease in  $J$ , the  $P$  branch, and those with no change in  $J$ , the central  $Q$  branch. For all heteronuclear diatomics and certain vibrations of linear polyatomics, the  $Q$  branch is absent (see top frame in fig. 9). Because molecules are not free to rotate in most ices at 10 K, the lines which make up the familiar  $P$  and  $R$  branches collapse into one broad band which corresponds to the pure vibration. This is illustrated in fig. 9. In the upper frames the spectrum of gas phase CO is shown at different spectral resolutions. At  $2\text{ cm}^{-1}$  resolution, the rotational lines making up the  $P$  and  $R$  branches are resolved. At lower resolution, while the individual lines are no longer separable, the rotational profile due to the  $P$  and  $R$  branches is still recognizable. The spectrum of CO frozen in a molecular ice is

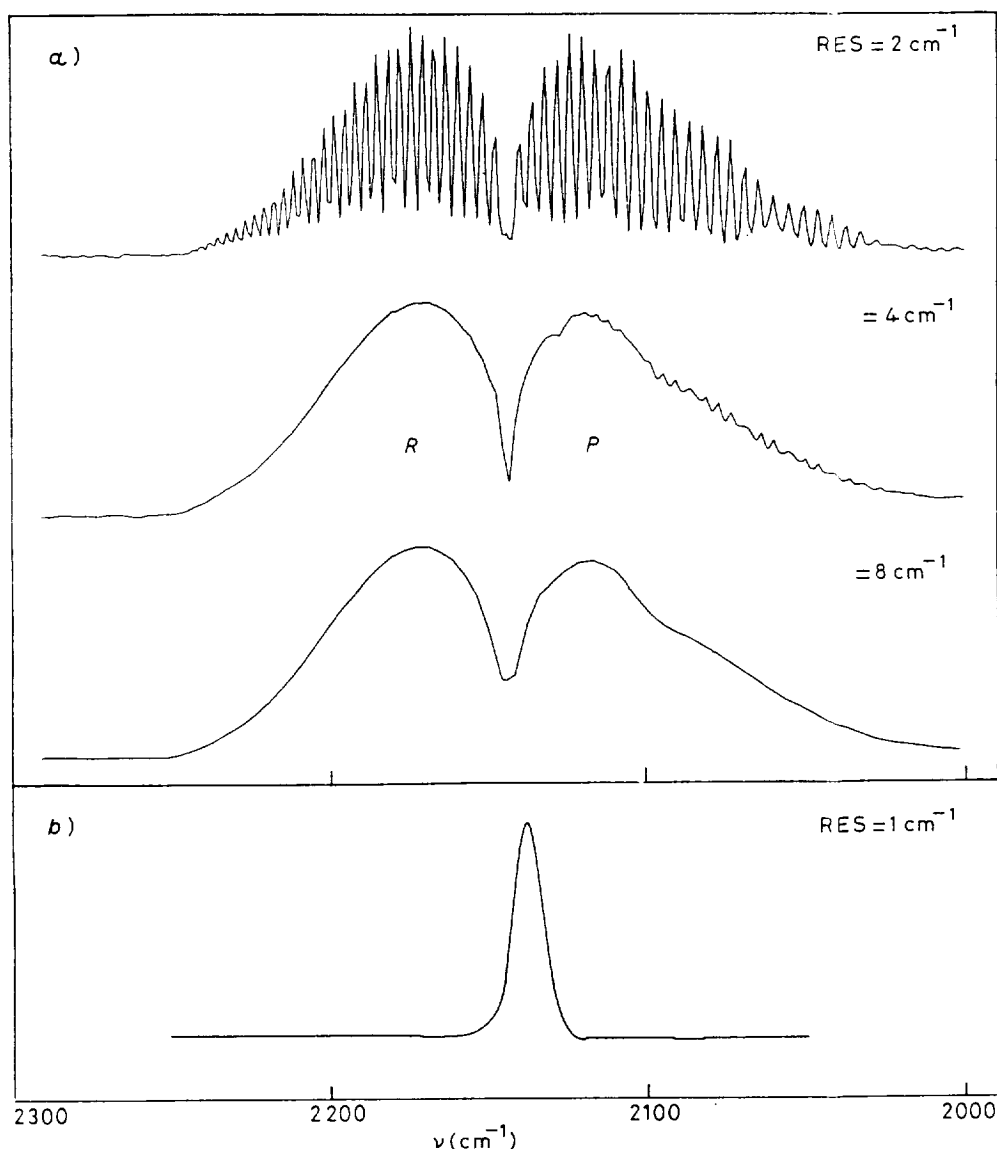


Fig. 9. – The infrared spectra of CO *a*) in the gas phase at 300 K and 20 mbar and *b*) in a mixed molecular ice solid mixture at 10 K, CO:H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub> (3:6:3:2). The spectral resolution is indicated by RES.

shown in the lower frame. Note that, in this case, the vibration occurs at nearly the same frequency as that of gas phase CO, *i.e.* in the null gap or missing *Q* branch region between 2135 and 2151 cm<sup>-1</sup>. Figures 8 and 9 illustrate how rotational-line suppression greatly simplifies the spectrum of a mixed molecular solid.

4.2.2. – Line broadening. In an amorphous, rather than crystalline, solid there is a substantial amount of irregularity in the structure [20]. Consequently, each molecule can be situated in a range of different sites. Because of inter-

actions with the environment which are due to a combination of dispersive, steric (geometrical) and dipolar forces, the vibrational frequencies of a molecule in one site can be different from that for the same kind of molecule in another site. Since the spectrum samples a large number of molecules in many different sites, and there is a distribution of sites, a broadened band is produced. Such heterogeneous broadening can range from a few wave numbers to several hundred wave numbers, depending on the nature of the interaction and range of sites. For a relatively nonpolar molecule such as CO the full width at half maximum spans the range from less than 1 to about 15 wave numbers. For a strongly hydrogen-bonded molecule such as H<sub>2</sub>O, the FWHM can vary from less than one wave number in a nonpolar solvent to over three hundred wave numbers in amorphous solid H<sub>2</sub>O [12,15].

4.2.3. – Line shifting. Shifts from the free gas phase frequency also arise from interactions between the vibrating molecule and the surroundings. Line shifting (and broadening) is caused by the influence neighboring species have on the bond force constant for the particular vibration under consideration. As with line broadening, the stronger the interaction, the greater the shift. The magnitude of this effect can vary over a large range. In solid CO, for example, the CO stretch occurs at 2138 cm<sup>-1</sup>, about 5 cm<sup>-1</sup> lower than the 0-0 transition for gaseous CO, while in an H<sub>2</sub>O/CH<sub>3</sub>OH/NH<sub>3</sub>/CO=20/10/1/1 mixture, it is shifted to 2137 cm<sup>-1</sup> [19]. This rather small shift indicates that there is only a weak interaction between CO and even such strongly polar molecules such as H<sub>2</sub>O and NH<sub>3</sub>. For molecules which can form weak chemical complexes, or even stronger hydrogen bonds (H bonds), the shift can be much larger [47]. For H<sub>2</sub>O, the shift can be greater than 300 cm<sup>-1</sup>, as shown in fig. 8. Different fundamental vibrations in the same molecule are generally affected differently. For example, as also illustrated in fig. 8, the fundamental OH stretching frequency in H<sub>2</sub>O undergoes a very large shift from 3707 cm<sup>-1</sup> to about 3300 cm<sup>-1</sup> and severe line broadening from less than 1 cm<sup>-1</sup> to over 300 cm<sup>-1</sup> upon condensation in an H<sub>2</sub>O-rich ice, while the H-O-H bend in the same molecule is far less affected: the shift is only tens of wave numbers, while the width is increased from less than 1 cm<sup>-1</sup> to about 50 cm<sup>-1</sup>.

4.3. *The IR spectrum of H<sub>2</sub>O ice.* – As an interesting application of these principles and because of its importance in astrophysics, the well-known behavior of the OH stretching mode of H<sub>2</sub>O, with particular emphasis on the large frequency shift, will be presented in some detail [14, 15]. When suspended in a nonpolar solid (*e.g.*, a CO matrix) H<sub>2</sub>O molecules are isolated and do not interact directly with each other and only weakly with the matrix. In this case the OH stretch falls at 3707 cm<sup>-1</sup>,  $\approx 50$  cm<sup>-1</sup> lower than in the gas phase. If the CO is removed, H bond formation between the H atoms of one H<sub>2</sub>O molecule with the oxygen atom of an adjacent molecule will occur. This attraction of the



H atom by another  $\text{H}_2\text{O}$  molecule causes a substantial reduction of the bond force constant and a correspondingly large shift (nearly  $500\text{ cm}^{-1}$ ) of the OH stretch to lower frequencies. Of course, an amorphous  $\text{H}_2\text{O}$  structure consists of a wide variety of interaction geometries and strengths which give rise to an extremely broad band ( $\text{FWHM} \approx 300\text{ cm}^{-1}$ ). This behavior is shown in fig. 10. The lower trace shows the spectrum for the mixture  $\text{CO}/\text{H}_2\text{O} = 9/1$  in which nearly all of the  $\text{H}_2\text{O}$  molecules are isolated. The absorptions at  $3707$  and  $3673\text{ cm}^{-1}$  are due to  $\text{H}_2\text{O}$  monomers and dimers, respectively [48]. Upon warm-up to  $30\text{ K}$ , diffusion occurs permitting some of the  $\text{H}_2\text{O}$  molecules to form H bonds, as shown by the increase in absorption due to dimers and higher polymers in the second spectrum. This process continues as the sample is warmed up to even higher temperatures and the CO evaporates. Note also that the absorption coefficient per  $\text{H}_2\text{O}$  molecule undergoes a substantial, anomalous increase as  $\text{H}_2\text{O}$  goes from the monomeric to the ice form [49].

Further shifting and broadening can occur if  $\text{H}_2\text{O}$  interacts with a chemical base, such as  $\text{NH}_3$  [15]. In acid-base terminology,  $\text{H}_2\text{O}$  is neutral and, in the presence of a base, at least one of the hydrogen atoms of  $\text{H}_2\text{O}$  will form a complex with this base. This H atom will experience an attractive force greater than it would have when H-bonding with another  $\text{H}_2\text{O}$  molecule, and thus the OH stretching frequency will be even further redshifted than in pure  $\text{H}_2\text{O}$  ice. In the case of  $\text{H}_2\text{O}-\text{NH}_3$  mixtures, the shift is on the order of  $800\text{ cm}^{-1}$  and the band is again a few hundred wave numbers wide. A mixture consisting of comparable amounts of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  will be made up of some  $\text{H}_2\text{O}$  molecules

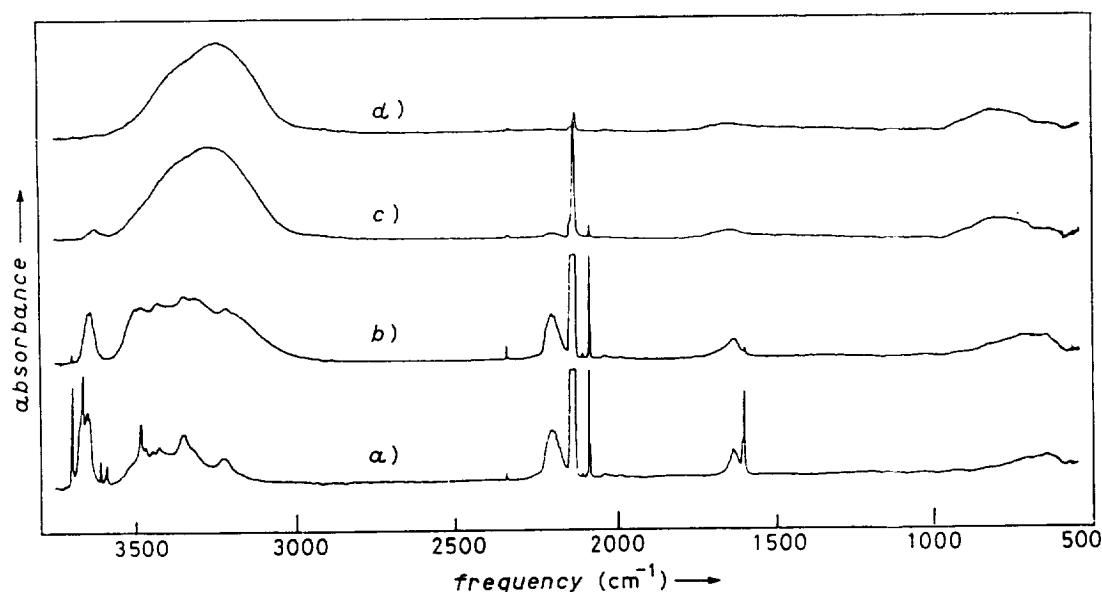


Fig. 10. – The evolution of the infrared absorbance spectrum of an  $\text{H}_2\text{O}:\text{CO}$  (1:9) mixture as the sample is warmed up from  $10\text{ K}$ . All spectra are plotted on the same absorbance scale. From bottom to top: a) immediately after deposition at  $10\text{ K}$ ; b) after warm-up to  $30\text{ K}$  without  $\text{CO}$  evaporation; c), d) after  $\text{CO}$  evaporation above  $30\text{ K}$  (taken from [48]).

TABLE II. — *Infrared integrated absorbance values for molecules of astrophysical interest in the solid state.*

Molecule	Mode	Frequency (cm <sup>-1</sup> )	$\lambda$ ( $\mu$ m)	A (cm/molecule)
H <sub>2</sub> O <sup>(a)</sup>	OH stretch	3257	3.07	2 (– 16)
	OH bend	1670	6.00	8 (– 18)
	libration	750	13.3	3 (– 17)
CO	stretch in CO <sup>(b)</sup>	2139	4.675	1 (– 17)
	stretch in H <sub>2</sub> O <sup>(c)</sup>	2136	4.680	2 (– 17)
CO <sub>2</sub> <sup>(d)</sup>	stretch in CO <sub>2</sub>	2343	4.268	8 (– 17)
	stretch in H <sub>2</sub> O	2342	4.270	2 (– 16)
	bend in CO <sub>2</sub>	660, 665	15.2, 15.3	1 (– 17)
	bend in H <sub>2</sub> O	653	15.3	4 (– 17)
CH <sub>4</sub> <sup>(e)</sup>	CH stretch	3010	3.322	6 (– 18)
	CH deformation	1300	7.692	6 (– 18)
NH <sub>3</sub> <sup>(e)</sup>	NH stretch	3375	2.963	1 (– 17)
	umbrella	1070	9.346	2 (– 17)
CH <sub>3</sub> OH <sup>(e)</sup>	OH stretch	3250	3.077	1 (– 16)
	CH stretch	2982	3.354	2 (– 17)
	CH stretch	2828	3.536	8 (– 18)
	CH and OH deformation	«1455»	«6.87»	1 (– 17)
	CO stretch	1026	9.747	2 (– 17)
hexane <sup>(e,f)</sup>	CH stretch <sup>(g)</sup>	2955	3.384	1 (– 17)
		2870	3.484	2 (– 18)
	CH stretch <sup>(h)</sup>	2921	3.424	5 (– 18)
		2858	3.499	1 (– 18)
	CH deformation <sup>(i)</sup>	«1465»	«6.83»	1 (– 18)
	CH deformation <sup>(g)</sup>	1370	7.299	2 (– 19)
CH <sub>3</sub> CN <sup>(e)</sup>	CN stretch	2270	4.405	2 (– 18)
ethyl-acetate <sup>(e,j)</sup>	C=O stretch	1738	5.754	4 (– 17)
	CH stretch <sup>(g)</sup>	2986	3.349	2 (– 18)
	CH <sub>2</sub> deformation <sup>(h)</sup>	1450	6.897	8 (– 18)
	CH <sub>3</sub> deformation <sup>(g)</sup>	1375	7.273	4 (– 18)

(a) Ref. [14, 15]; (b) ref. [50]; (c) ref. [19]; (d) ref. [51], absorption strength in CO similar, but peak positions slightly shifted; (e) ref. [18]; (f) CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>; (g) per —CH<sub>3</sub> group; (h) per —CH<sub>2</sub>— group; (i) per —CH<sub>3</sub> and —CH<sub>2</sub>— group; (j) CH<sub>3</sub>(CO)OCH<sub>2</sub>CH<sub>3</sub>.

H-bonded to other  $\text{H}_2\text{O}$  molecules and some forming acid complexes with the  $\text{NH}_3$ . Since absorption due to both forms of  $\text{H}_2\text{O}$  is so broad, the absorption band will be a blend of the two. Because the base- $\text{H}_2\text{O}$  complex absorption is shifted more than the H-bonded  $\text{H}_2\text{O}$  band, the overall band will resemble that due to amorphous  $\text{H}_2\text{O}$  distorted by a wing on the long-wavelength side [15]. The absorption strength of the wing with respect to that of the  $3250\text{ cm}^{-1}$  component will depend upon how much of each species is present. Note that such a long-wavelength wing only implies the presence of a base, not necessarily  $\text{NH}_3$ .

4.4. *Column density determination.* – The column density of an individual component or type of molecular subgroup in an interstellar ice can only be determined for species in which the integrated absorbance,  $A$ , has been measured in an appropriate matrix. The column density of any solid-state species can be estimated by

$$(2) \quad N = \frac{\tau_{\max} \Delta\nu_{1/2}}{A},$$

where  $\tau_{\max}$  is the optical depth of the band at maximum absorbance,  $\Delta\nu_{1/2}$  the FWHM (in  $\text{cm}^{-1}$ ) and  $A$ , the integrated absorbance (in  $\text{cm molecule}^{-1}$ ). Table II lists integrated absorbance values for several astrophysically relevant molecules in the solid state.

This technique has been applied to various absorption bands in protostellar spectra to determine the column density of CO, CN,  $\text{H}_2\text{O}$  and aliphatic carbon ( $-\text{CH}_3$  and  $-\text{CH}_2-$ ) groups on the grains towards these sources [9, 19, 52-54]. The use of this equation will be illustrated by reviewing the calculations of the column density of CO frozen in the icy grain mantles along the line of sight to NGC 7538-IRS 9. The solid-CO band in this source shows evidence for two components, a relatively narrow one at  $2140\text{ cm}^{-1}$  and a broader one at  $2136\text{ cm}^{-1}$ . For the  $2140\text{ cm}^{-1}$  component,  $\tau_{\max} = 2.09$  and  $\Delta\nu_{1/2} \approx 5.0\text{ cm}^{-1}$  has been measured [53]. Substituting these values into eq. (2) and using  $A = 10^{-17}\text{ cm molecule}^{-1}$  appropriate for pure CO (see table II), the solid-CO column density is calculated to be  $10^{18}\text{ molecules cm}^{-2}$ . Adding the contribution for the broader  $2136\text{ cm}^{-1}$  component, attributed to CO isolated in an  $\text{H}_2\text{O}$  matrix (see subsect. 5.1), yields a total solid-CO column density of  $1.8 \cdot 10^{18}\text{ molecules cm}^{-2}$ .

## 5. – The composition of interstellar icy grain mantles.

5.1. *IR spectroscopy of protostars.* – Many objects embedded in or located behind a dense molecular cloud show deep absorption features at 3.08, 4.67, 6.85

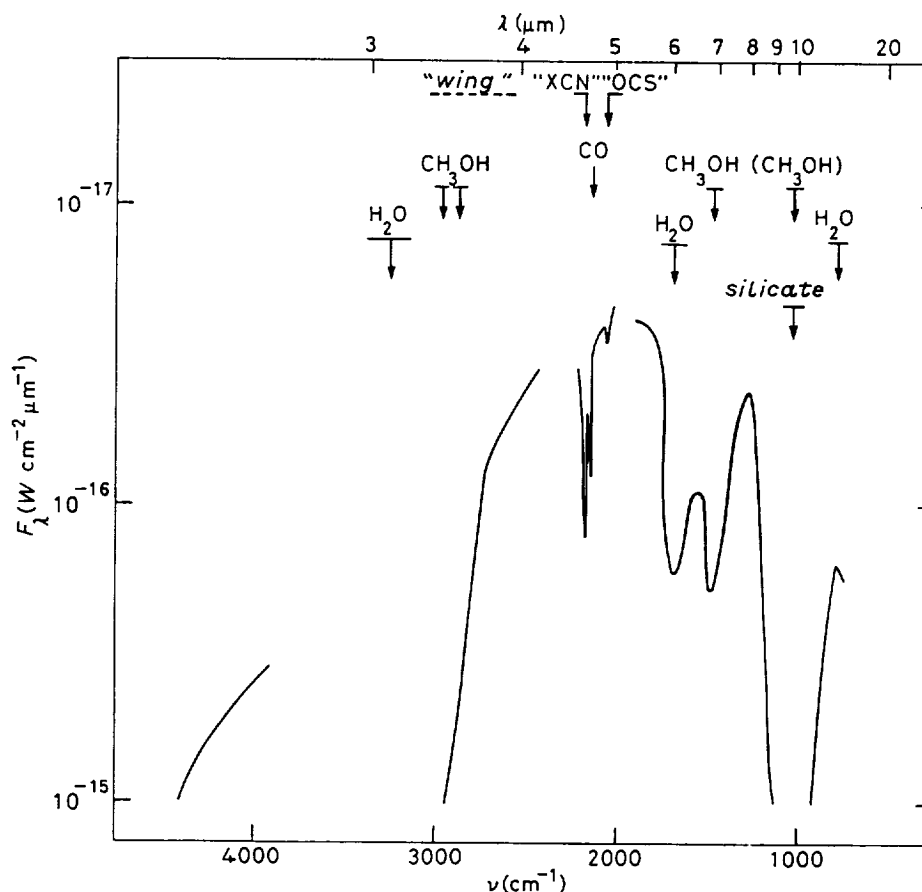


Fig. 11. – The infrared spectrum of the protostar W33A. Identifications for the observed absorption features in terms of simple «icy» molecules are indicated on the top (see ref. [13]). Some of these are, however, not unequivocally accepted. The deep 10  $\mu\text{m}$  band is generally attributed to refractory silicates. See text for details.

and 10  $\mu\text{m}$  (3250, 2140, 1670 and 1460  $\text{cm}^{-1}$ )(\*) in their spectrum [13, 22]. Figure 11 shows the composite IR spectrum of one of the best-studied objects, W33A. With the exception of the 10  $\mu\text{m}$  (1000  $\text{cm}^{-1}$ ) band, these features are generally attributed to simple molecules embedded in icy grain mantles along the line of sight. Proposed identifications for these absorption features have recently been reviewed by [13] and only some new developments will be discussed here.

5.1.1. The 3.08  $\mu\text{m}$  (3250  $\text{cm}^{-1}$ ) band. – The strong band at 3.08  $\mu\text{m}$  (3250  $\text{cm}^{-1}$ ) is due to the OH stretching vibration of  $\text{H}_2\text{O}$  ice or mixtures dominated by  $\text{H}_2\text{O}$ . Recent studies have shown that the detailed shape of this

(\*) Throughout the rest of this section band positions will be given in micrometers as well as wave numbers, since in the astrophysical literature absorption features are often (confusingly) named after their wavelength position.

band is severely influenced by scattered light [55, 56]. This is particularly true for the  $2.97\text{ }\mu\text{m}$  ( $3370\text{ cm}^{-1}$ ) shoulder on this band, which was previously ascribed to  $\text{NH}_3$  [24, 57], but which is now thought to result (mainly) from scattering by large ice grains.

The  $3.08\text{ }\mu\text{m}$  ( $3250\text{ cm}^{-1}$ ) ice band shows a low-frequency wing, whose origin is unclear. It is probably not due to scattering by large particles [58] as evidenced by the polarization study of BN [59]. This wing has also been attributed to absorption by  $\text{H}_2\text{O}$  hydrogen-bonded to strong bases such as  $\text{NH}_3$  [57, 59], but the upper limit on the  $\text{NH}_3$  abundance itself is quite small and this base cannot be responsible [13, 24]. Alternatively, this wing may be caused by overlapping CH stretching absorption features due to organic molecules mixed in with the ice. Indeed, recent higher-resolution studies of W33A as well as other protostars have revealed substructure at about  $3.5\text{ }\mu\text{m}$  ( $2860\text{ cm}^{-1}$ ) which is well matched in detail with the CH stretching vibration of  $\text{CH}_3\text{OH}$  (fig. 12 [60]). More substructure is present in these spectra, perhaps indicating many blended CH stretching modes in a family of organic compounds. However, this view is not universally accepted and further high-resolution observations of a larger sample of objects will be very important to resolve this issue.

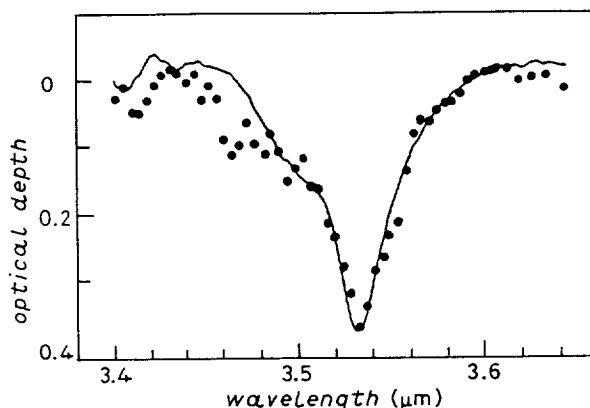


Fig. 12. – A weak feature at about  $3.5\text{ }\mu\text{m}$  has been detected in the spectrum of W33A (dots [60]). It seems to be present in the spectra of other sources as well. A good match to the shape of this feature is obtained with solid  $\text{CH}_3\text{OH}$  (solid line).

5.1.2. – The  $4.62\text{ }\mu\text{m}$  ( $2160\text{ cm}^{-1}$ ) band. The  $4$  to  $5\text{ }\mu\text{m}$  ( $(2500 \div 2000)\text{ cm}^{-1}$ ) region is very characteristic of triple bond and cumulative double-bond vibrations. W33A shows a strong band at  $4.62\text{ }\mu\text{m}$  ( $2160\text{ cm}^{-1}$ ), which has been assigned to the  $\text{C}\equiv\text{N}$  stretching mode [53, 61]. A direct comparison with the laboratory spectrum of a specific candidate molecule has not yet been made. Laboratory UV photolysis studies of simple molecular mixtures containing carbon, nitrogen and oxygen often show a strong absorption feature at this wavelength which matches the observed interstellar feature very well (fig. 13 [53]). An identification of the carrier as a nitrile or

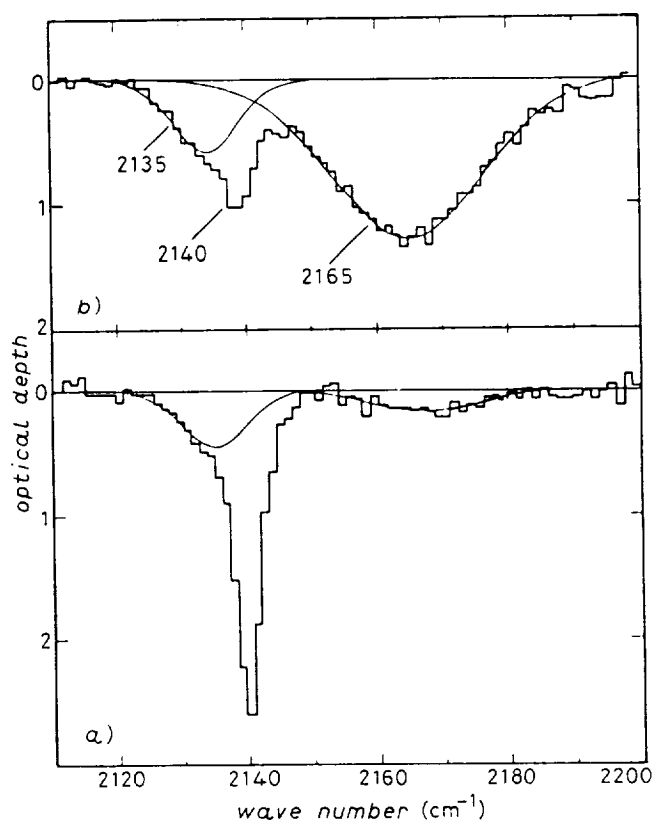


Fig. 13. – The laboratory spectrum in the  $(2100 \div 2200) \text{ cm}^{-1}$  region of an  $\text{NH}_3/\text{CO}$  ice which has been photolyzed and warmed up to 150 K compared to the spectrum of a) NGC 7538/IRS9, b) W33A. Figure adapted from ref. [53].

isonitrile seems reasonable [9]. It has also been suggested that the laboratory feature, and by inference the interstellar feature, is actually due to the  $\text{OCN}^-$  ion [62]. In salts, this ion shows an absorption feature at about this wavelength, although the exact peak position depends strongly on the cation present. However, no positive evidence for the presence of this anion in the laboratory photolysis studies has been presented. Moreover, the peak frequency of an absorption feature due to an ion will be very sensitive to the local matrix environment (*i.e.* cation, degree of solvation). Yet the measured laboratory peak frequency does not shift upon warm-up,  $\text{H}_2\text{O}$  ice evaporation and organic-residue formation. Clearly, the carrier of this laboratory band cannot be an ion and further laboratory studies are required to identify it. Finally, it has been suggested that the interstellar  $4.62 \mu\text{m}$  ( $2160 \text{ cm}^{-1}$ ) band is actually due to the SiH stretching vibration in organic silicon compounds [63]. Such molecular structures may result from UV photolysis of icy molecules containing silicon compounds (*e.g.*,  $\text{SiH}_4$ ). A detailed comparison of these laboratory spectra with the observations could be very interesting.

5.1.3. – The  $4.67\ \mu\text{m}$  ( $2140\ \text{cm}^{-1}$ ) band. Many sources show a strong, narrow absorption feature near  $4.67\ \mu\text{m}$  ( $2140\ \text{cm}^{-1}$ ), which is commonly attributed to solid CO (fig. 13 [53, 54, 61, 64]). Most observed spectra show a narrow ( $0.01\ \mu\text{m}$ ,  $4\ \text{cm}^{-1}$ ) component at  $\approx 4.67\ \mu\text{m}$  ( $2140\ \text{cm}^{-1}$ ). Sometimes, a long-wavelength wing, probably due to a broad ( $\approx 0.02\ \mu\text{m}$ ,  $9\ \text{cm}^{-1}$ ), weak, underlying component ( $\approx 4.68\ \mu\text{m}$ ,  $2136\ \text{cm}^{-1}$ ), is also present. In a few cases an increased width or shifted peak position indicates a different mix [64].

Laboratory studies show that the peak position and shape of the fundamental vibration of CO mixed into cold, molecular ices is a complex function of its interaction with the surrounding matrix (fig. 14 [19]). Among the possible effects are electrostatic dipole-induced dipole interaction as for  $\text{H}_2\text{O}/\text{CO}$  complexes [48], the presence of substitutional as well as interstitial sites as in disordered amorphous ices [19] and electron donation by surrounding strong bases [65]. The absorption feature due to CO molecules isolated in a matrix by  $\text{H}_2\text{O}$  occurs at about  $4.68\ \mu\text{m}$  ( $2136\ \text{cm}^{-1}$ ) and has a width of about  $0.02\ \mu\text{m}$  ( $10\ \text{cm}^{-1}$ ). Pure solid CO absorbs at about  $4.675\ \mu\text{m}$  ( $2139\ \text{cm}^{-1}$ ) with a width of about  $0.005\ \mu\text{m}$  ( $1\ \text{cm}^{-1}$ ). Doping of the CO matrix with traces of other species leads to a broadening but little shift of this line. Since the observed

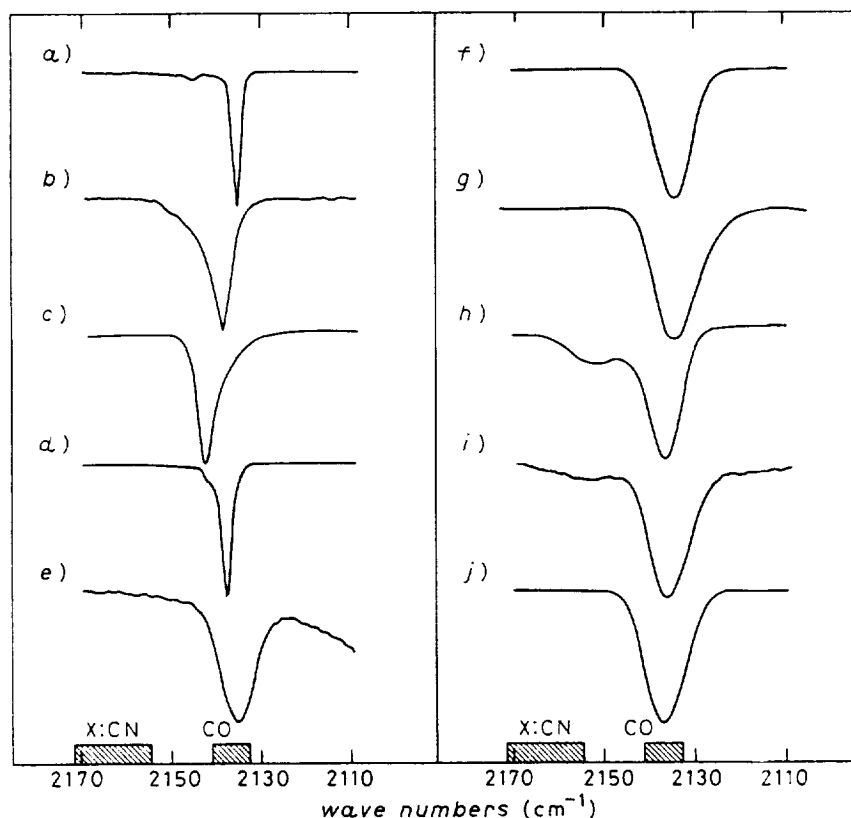


Fig. 14. – The CO stretching mode for CO suspended in various molecular mixtures at 10 K: a)  $\text{CH}_4:\text{CO}$  (20:1), b)  $\text{CO}_2:\text{CO}$  (20:1), c)  $\text{C}_2\text{H}_2:\text{CO}$  (20:1), d) pure CO, e)  $\text{OCS}:\text{CO}$  (20:1), f)  $\text{H}_2\text{S}:\text{CO}$  (20:1), g)  $\text{NH}_3:\text{CO}$  (20:1), h)  $\text{H}_2\text{O}:\text{CO}$  (20:1), i)  $\text{CH}_3\text{COCH}_2:\text{CO}$  (20:1), j)  $\text{CH}_2\text{CN}:\text{CO}$  (20:1). Adapted from ref. [19].

$3.08\mu\text{m}$  ( $3250\text{ cm}^{-1}$ ) ice band attests to the presence of  $\text{H}_2\text{O}$ -dominated ice mantles, it is tempting to attribute the observed, relatively broad, underlying CO component to CO in  $\text{H}_2\text{O}$ -dominated grain mantles, while the narrow CO component may be due to more pure CO ices containing little  $\text{H}_2\text{O}$ . Indeed, a reasonable fit to the narrow interstellar component can be obtained with pure CO [64]. Thus these CO observations do reveal, for the first time, the presence of at least two distinct grain mantle components along the same line of sight in interstellar clouds.

5.1.4. – The  $6.0$  and  $6.85\mu\text{m}$  ( $1670$  and  $1460\text{ cm}^{-1}$ ) bands. The  $(5 \div 8)\mu\text{m}$  ( $(2000 \div 1250)\text{ cm}^{-1}$ ) region is characteristic for CH, NH and OH bending and deformation modes and the strong carbonyl ( $\text{C}=\text{O}$ ) stretching mode. Two absorption features, at  $6.0$  and  $6.85\mu\text{m}$  ( $1670$  and  $1460\text{ cm}^{-1}$ ), have been detected in this wavelength region in protostellar objects. These have been attributed to the OH bending mode in  $\text{H}_2\text{O}$  and the CH deformation mode in  $\text{CH}_3\text{OH}$ , respectively [52]. Some low-resolution ( $\lambda/\Delta\lambda \approx 50$ ), interstellar spectra have shown evidence for spectral structure in this wavelength region which has been interpreted in terms of carbonyl-bearing molecules such as  $\text{H}_2\text{CO}$  [13]. Recent moderate-resolution ( $\lambda/\Delta\lambda \approx 150$ ) spectra obtained with the KAO are in good agreement with previous lower-resolution spectra (fig. 15). The features in the spectrum of W33A are indeed fitted very well by laboratory spectra of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  (fig. 15). The latter identification is, however, not unequivocally accepted (see below). Carbonyl-bearing molecules (*e.g.*,  $\text{H}_2\text{CO}$ ) show strong  $\text{C}=\text{O}$  stretching vibration at about  $5.8\mu\text{m}$  ( $1720\text{ cm}^{-1}$ ). The smoothness of the  $6.0\mu\text{m}$  ( $1670\text{ cm}^{-1}$ ) feature in W33A implies an upper limit of about 0.2% on the abundance of  $\text{C}=\text{O}$  groups with respect to  $\text{H}_2\text{O}$ .

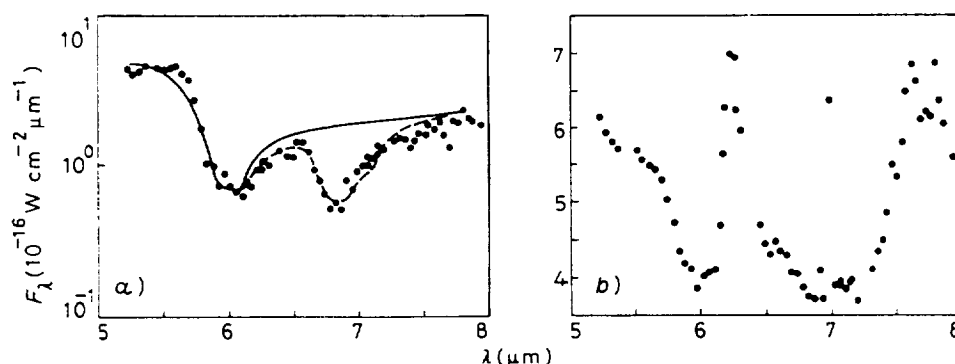


Fig. 15. – Recent  $(5 \div 8)\mu\text{m}$  spectra of two protostars: *a*) W33A, —  $\text{H}_2\text{O}$ , ---  $\text{CH}_3\text{OH}$ ; *b*) Mon R2-IRS2. W33A shows absorption features at  $6.0$  and  $6.85\mu\text{m}$  ( $1670$  and  $1460\text{ cm}^{-1}$ ) which are particularly well matched by the laboratory spectra of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ , respectively. Although a weak  $6.0\mu\text{m}$  absorption feature may be present, the spectrum of Mon R2-IRS2 is dominated by the well-known  $6.2$  and  $7.7\mu\text{m}$  emission features due to PAH molecules and the Ar II and Pf $\alpha$  emission lines. Recognition of these emission components in previous studies was hampered by insufficient resolution.



The spectrum of Mon R2-IRS 2 is strikingly different from that of W33A. Rather than the presence of carbonyl groups as previously suggested [52], these higher-resolution observations show that this is due to the presence of strong PAH emission features at 6.2, 7.7, and probably 5.2  $\mu\text{m}$  (1610, 1300, and 1920  $\text{cm}^{-1}$ ). Note that the 7.7  $\mu\text{m}$  feature in this source is particularly well resolved in the well-known components at about 7.5 and 7.8  $\mu\text{m}$  (1330 and 1280  $\text{cm}^{-1}$  [66]). The Ar II line at 6.99  $\mu\text{m}$  is also obvious at this resolution. These emission features probably arise in the nearby compact H II region associated with Mon R2-IRS 1. Although a narrow 6.0  $\mu\text{m}$  (1670  $\text{cm}^{-1}$ ) absorption band similar to that in W33A seems to be present in this source, there is little evidence for a 6.85  $\mu\text{m}$  (1460  $\text{cm}^{-1}$ ) absorption band.

Perhaps not surprising, the Leiden group has recently suggested that, like their assignment of the 4.62  $\mu\text{m}$  (2160  $\text{cm}^{-1}$ ) band, the 6.85  $\mu\text{m}$  (1460  $\text{cm}^{-1}$ ) band is also due to an ion produced by UV photolysis (*i.e.*  $\text{R-NH}_3^+$  or  $\text{NH}_4^+$  [34, 67]). Laboratory UV photolysis studies on  $\text{NH}_3/\text{O}_2$  mixtures demonstrate that a simple nitrogen and/or oxygen containing compound produces an absorption feature around 6.7  $\mu\text{m}$  (1490  $\text{cm}^{-1}$ ). A similar band appears upon UV photolysis of a  $\text{H}_2\text{O}/\text{NH}_3/\text{CO}/\text{O}_2$  (10/1/1/1) mixture, which by inference is then attributed to the same compound. This band shows considerable shift upon warm-up, consistent with ion solvation (or annealing) effects. A good fit to the interstellar band can be obtained with a sample warmed up to 180 K [67]. However, similar processing of other equally relevant interstellar mixtures does not provide such a good agreement [9, 34]. The temperature sensitivity is also difficult to reconcile with the similarity in the 6.85  $\mu\text{m}$  (1460  $\text{cm}^{-1}$ ) profile observed in a variety of sources. Indeed, the shape of this band in W33A, NGC 7538-IRS 9, W3 IRS 5 and AFGL 2136 is very similar despite the large difference in optical depth [13]. In contrast, the invariance of the shape is readily understood assuming  $\text{CH}_3\text{OH}$  absorption. This and the detection of the 3.5  $\mu\text{m}$  (2860  $\text{cm}^{-1}$ ) absorption (see fig. 12) makes  $\text{CH}_3\text{OH}$  the preferred interpretation in the authors' opinion.

5.2. *Grain mantle abundances.* – Table III summarizes typical abundances for several interesting molecules in interstellar icy grain mantles relative to  $\text{H}_2\text{O}$ . This molecule always has the largest column density along a line of sight. However, as discussed above, the solid-CO data imply the existence of at least two, distinctly different grain mantle components along many lines of sight. Typical estimates for the solid-CO abundance in these two components are listed separately in table III. Although many questions remain, a suggestive comparison can be made between observed and calculated abundances (table III). For example, several of the molecules predicted to be present have been observed with approximately the right abundance. The detection of grain mantles dominated by nonpolar molecules, rather

TABLE III. – *Composition of interstellar icy grain mantles.*

Species	Absorption features		Abundance ( <sup>1</sup> )	
	$\lambda(\mu\text{m})$	$\nu(\text{cm}^{-1})$	Observed	Calculated ( <sup>2</sup> )
H <sub>2</sub> O	3.08	3250	—	—
	6.00	1650	100	100
CO ( <sup>3</sup> )	4.68	2135	0 ÷ 5	0.4
	4.67	2140	0 ÷ 25	—
CH <sub>3</sub> OH	3.5	2830	7 ( <sup>4</sup> )	(40) ( <sup>5</sup> )
	6.85	1460	50	—
XCN	4.61	2167	(4) ( <sup>6</sup> )	—
OCS	4.90	2040	(0.05) ( <sup>7</sup> )	0.4
NH <sub>3</sub>	2.95	3375	< 5	1
	6.10	1625	—	—
H <sub>2</sub> S	3.94	2540	0.3	0.03
CH <sub>4</sub>	7.70	1300	< 1	0.007
H <sub>2</sub> CO	3.53	2835	< 0.2	(0) ( <sup>5</sup> )
	5.80	1720	—	—
CO <sub>2</sub>	4.28	2337	— ( <sup>8</sup> )	9

(1) Abundances of molecules in grain mantles relative to H<sub>2</sub>O = 100.

(2) Calculated abundances for a reducing atmosphere ( $n_0 = 10^4 \text{ cm}^{-3}$  [24]).

(3) The 4.68 and 4.67  $\mu\text{m}$  bands refer to the two independent CO components observed. Both abundance estimates are relative to the total H<sub>2</sub>O (ice) column density along the line of sight.

(4) The observed abundance of CH<sub>3</sub>OH is controversial (see text).

(5) Assuming all H<sub>2</sub>CO converted into CH<sub>3</sub>OH by grain surface reactions.

(6) Thought to result from UV photolysis. Abundance estimated from laboratory studies.

(7) Assuming absorption is due to OCS.

(8) Presently unobservable due to telluric CO<sub>2</sub>.

than H<sub>2</sub>O, is also in good agreement with theoretical predictions. The detection of oxygen-rich interstellar grain mantles (*i.e.* CO<sub>2</sub>, O<sub>3</sub>) probably has to await space-borne IR spectrometers on ISO and SIRTf.

There is some controversy on the abundance of CH<sub>3</sub>OH. The abundance inferred from the 3.5  $\mu\text{m}$  (2860  $\text{cm}^{-1}$ ) band is much lower than that obtained from the 6.85  $\mu\text{m}$  (1460  $\text{cm}^{-1}$ ) band and may imply that the latter is largely due to molecules other than CH<sub>3</sub>OH [60]. However, part of this discrepancy may actually reflect the uncertainty in the underlying continuum of the 3.5  $\mu\text{m}$

( $2860\text{ cm}^{-1}$ ) band due to the low-frequency wing of the  $3.08\text{ }\mu\text{m}$  ( $3250\text{ cm}^{-1}$ ) ice band and the blending of overlapping CH stretching bands (see paragraph 5.1.1). Moreover, in a circumstellar disk/scattering nebula geometry, the ratio of absorption features in different parts of the spectrum can be distinctly different from their intrinsic value [56]. Essentially, near-infrared photons preferentially result from scattering into the beam of photons «escaping» through the poles, while mid-infrared photons are directly emitted into the beam by the stellar (or dust) photosphere. As a result, the near-infrared wavelength photons will encounter less absorption than expected from the strength of mid-infrared absorption features. Since most protostars seem to be embedded in near-infrared reflection nebulae and the shape of the  $3.08\text{ }\mu\text{m}$  ( $3250\text{ cm}^{-1}$ ) feature is often affected by scattering, this is probably a common effect. Indeed, the ratio of the  $3.08\text{ }\mu\text{m}$  to the  $6.0\text{ }\mu\text{m}$  band, both generally attributed to  $\text{H}_2\text{O}$ , is observed to vary by a factor 3 from source to source [13]. In the analysis of grain mantle abundances (table III) we have, therefore, relied on column densities derived from the mid-infrared absorption features.

5.3. *Organic refractory grain mantles.* – It is of some interest to consider the observational constraints on the abundance of the organic refractory grain mantles resulting from the irradiation of these icy mixtures. Laboratory studies suggest that about 1% by mass of the original ice mixture is converted into such a residue in one irradiation-warm-up cycle [34]. Since over the lifetime of a cloud many such cycles would occur, as much as 30% of all the carbon is then expected to be locked up in organic refractory grain mantles [20]. This seems excessive, since the IR spectra of protostars are dominated by simple ices (see subsect. 5.1), containing typically only 5% of the O and perhaps an equal amount of C, rather than by organic residues. In particular, presently, only the  $4.62\text{ }\mu\text{m}$  band is generally attributed to UV photolyzed grain mantles. All other observed absorption features are reasonably well accounted for by species produced by accretion and surface reactions. Absorption features due to organic residues in the  $3\text{ }\mu\text{m}$  region of interstellar spectra may be «hidden» to some extent by the strong  $3.08\text{ }\mu\text{m}$  ( $3250\text{ cm}^{-1}$ ) ice band. However, the  $(5\div 8)\text{ }\mu\text{m}$  laboratory spectra of such residues [9, 34] also show various strong absorption bands, which are not obvious in interstellar spectra. It seems that organic residues are not as abundant as these laboratory experiments suggest and may contain perhaps up to 5% of the elemental C or O. Further high-quality spectroscopic studies of protostars are of utmost importance to detect the weak bands and substructure expected to be associated with these organic residues.

## 6. – Summary.

Infrared absorption and emission spectroscopy of infrared continuum sources embedded in or behind dense molecular clouds provide a powerful

means of probing the composition of cosmic dust and the physical and chemical nature of the environments in which it is found. Comparison of laboratory absorption spectra of various materials with astronomical spectra indicates that the bulk of the absorption features associated with dark clouds are attributable to mixed molecular ices.  $\text{H}_2\text{O}$  dominates the composition of interstellar ices.  $\text{CH}_2\text{OH}$  may also be an important ice component. However, analysis of the various profiles and positions of the interstellar solid-CO feature near  $2140\text{ cm}^{-1}$  ( $4.67\text{ }\mu\text{m}$ ) suggests a more complex picture. Molecular clouds seem to contain at least two distinct types of ice; one characterized by polar, hydrogen-bonding molecules like  $\text{H}_2\text{O}$ , and the other characterized by nonpolar, or only slightly polar molecules, possibly CO itself. Such an interpretation would have been impossible without a great deal of prior laboratory work. Although many questions remain, a favorable—but nonunique—comparison can be made with the theoretical models which incorporate gas and grain-surface reactions. Finally, comparisons between the interstellar and laboratory spectra suggest that interstellar ices along some lines of sight also contain species which cannot be formed by simple gas-gas or gas-grain interactions. Probably these result from irradiation of the icy mixtures.

\* \* \*

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## REFERENCES

- [1] R. J. TRUMPLER: *Publ. Astron. Soc. Pac.*, **42**, 267 (1930).
- [2] D. R. HUFFMAN: *Adv. Phys.*, **26**, 129 (1977), and references therein.
- [3] M. H. MOORE, B. DONN, R. KHANNA and M. F. A'HEARN: *Icarus*, **54**, 388 (1983).
- [4] G. STRAZZULLA, V. PIRRONELLO and G. FOTI: *Astron. Astrophys.*, **123**, 93 (1983).
- [5] R. E. JOHNSON, L. J. LANZEROTTI, W. L. BROWN, W. M. AUGUSTYNIAK and C. MUSSIL: *Astron. Astrophys.*, **123**, 343 (1983).
- [6] L. J. LANZEROTTI, W. L. BROWN and R. E. JOHNSON: in *Ices in the Solar System*, edited by J. KLINGER, D. BENEST, A. DULLFUS and R. SMOLUCHOWSKI (Reidel, Dordrecht, 1984), p. 317.
- [7] R. E. JOHNSON, J. F. COOPER and L. J. LANZEROTTI: *Proceedings of the 20th ESLAB Symposium on Exploration of Halley's Comet*, ESA SP-250, Vol. II, 269 (1986).
- [8] W. HAGEN, L. J. ALLAMANDOLA and J. M. GREENBERG: *Astrophys. Space Sci.*, **65**, 215 (1979).
- [9] L. B. D'HENDECOURT, L. J. ALLAMANDOLA, R. J. A. GRIM and J. M. GREENBERG: *Astron. Astrophys.*, **158**, 119 (1986).
- [10] R. J. A. GRIM and J. M. GREENBERG: *Astron. Astrophys.*, **181**, 155 (1987).

- [11] L. J. ALLAMANDOLA, S. A. SANDFORD and G. J. VALERO: *Icarus*, **76**, 225 (1988).
- [12] L. J. ALLAMANDOLA: in *Galactic and Extragalactic Infrared Spectroscopy*, edited by M. KESLER and P. PHILIPS (Reidel, Dordrecht, 1984), p. 5.
- [13] A. G. G. M. TIELENS and L. J. ALLAMANDOLA: in *Physical Processes in Interstellar Clouds*, edited by G. E. MORFILL and M. SCHOLER (Reidel, Dordrecht, 1987), p. 333.
- [14] W. HAGEN, A. G. G. M. TIELENS and J. M. GREENBERG: *Chem. Phys.*, **56**, 367 (1981).
- [15] W. HAGEN, A. G. G. M. TIELENS and J. M. GREENBERG: *Astron. Astrophys., Suppl. Ser.*, **51**, 389 (1983).
- [16] K. KITTA and W. KRATSCHMER: *Astron. Astrophys.*, **122**, 105 (1983).
- [17] A. LÉGER, S. GAUTHIER, D. DEFOURNEAU and D. ROUAN: *Astron. Astrophys.*, **117**, 164 (1983).
- [18] L. B. D'HENDECOURT and L. J. ALLAMANDOLA: *Astron. Astrophys., Suppl. Ser.*, **64**, 453 (1986).
- [19] S. A. SANDFORD, L. J. ALLAMANDOLA, A. G. G. M. TIELENS and G. J. VALERO: *Astrophys. J.*, **329**, 498 (1988).
- [20] A. G. G. M. TIELENS and L. J. ALLAMANDOLA: in *Interstellar Processes*, edited by D. HOLLENBACH and H. THRONSON (Reidel, Dordrecht, 1987), p. 397.
- [21] L. J. ALLAMANDOLA and S. A. SANDFORD: in *Dust in the Universe*, edited by M. E. BAILEY and D. A. WILLIAMS (Cambridge University Press, Cambridge, 1988), p. 229.
- [22] A. G. G. M. TIELENS: in *Interstellar Dust*, edited by L. J. ALLAMANDOLA and A. G. G. M. TIELENS (Reidel, Dordrecht, 1989), p. 239.
- [23] W. M. IRVINE, P. F. GOLDSMITH and S. HJALMARSON: in *Interstellar Processes*, edited by D. HOLLENBACH and H. THRONSON (Reidel, Dordrecht, 1987), p. 561.
- [24] A. G. G. M. TIELENS and W. HAGEN: *Astron. Astrophys.*, **114**, 245 (1982).
- [25] A. G. G. M. TIELENS: *Astron. Astrophys.*, **119**, 177 (1983).
- [26] L. B. D'HENDECOURT, L. J. ALLAMANDOLA and J. M. GREENBERG: *Astron. Astrophys.*, **152**, 130 (1985).
- [27] P. D. BROWN, S. B. CHARNLEY and T. J. MILLAR: *Mon. Not. R. Astron. Soc.*, **231**, 409 (1988).
- [28] N. ZHAO: private communication (1989).
- [29] R. J. A. GRIM and L. B. D'HENDECOURT: *Astron. Astrophys.*, **167**, 161 (1986).
- [30] A. G. G. M. TIELENS and W. HAGEN: unpublished (1982).
- [31] A. DALGARNO and S. LEPP: *Astrophys. J. Lett.*, **287**, L47 (1985).
- [32] J. M. GREENBERG: in *Stars and Stellar Systems*, edited by B. WESTERLUND (Reidel, Dordrecht, 1979), p. 173.
- [33] L. B. D'HENDECOURT, J. L. ALLAMANDOLA, F. BAAS and J. M. GREENBERG: *Astron. Astrophys.*, **109**, L12 (1982).
- [34] W. SCHUTTE: Ph. D. Thesis, Rijksuniversiteit Leiden (1988).
- [35] S. S. PRASAD and S. P. TARAFDAR: *Astrophys. J.*, **267**, 603 (1983).
- [36] A. STERNBERG, A. DALGARNO and S. LEPP: *Astrophys. J.*, **320**, 676 (1987).
- [37] A. LÉGER, M. JURA and A. OMONT: *Astron. Astrophys.*, **144**, 147 (1985).
- [38] K. RÖSSLER: *Radiat. Eff.*, **99**, 21 (1986), and references therein.
- [39] G. C. PIMENTEL: in *The Formation and Trapping of Free Radicals*, edited by A. M. BASS and H. P. BROIDA (Academic Press, New York, N.Y. 1960), p. 69.
- [40] B. MEYER: *Low Temperature Spectroscopy* (Elsevier, Amsterdam, 1971).
- [41] H. E. HALLAM: *Vibrational Spectroscopy of Trapped Species* (Wiley & Sons, New York, N.Y., 1973).

- [42] G. OZIN and H. MOSCOVITZ: *Cryochemistry* (Wiley & Sons, New York, N.Y., 1976).
- [43] G. H. HERZBERG: *Infrared and Raman Spectra of Polyatomic Molecules* (van Nostrand Company, Princeton, N. J., 1968).
- [44] J. M. BARROW: *Introduction to Molecular Spectroscopy* (McGraw-Hill, New York, N.Y., 1962).
- [45] R. M. SILVERSTEIN and G. C. BASSLER: *Spectrometric Identification of Organic Compounds, Chapter 3: Infrared Spectrometry* (Wiley & Sons, New York, N.Y., 1967), p. 64.
- [46] L. J. BELLAMY: *The Infrared Spectra of Complex Organic Molecules* (Wiley & Sons, New York, N.Y., 1958).
- [47] G. C. PIMENTEL and A. L. MCCLELLAN: *The Hydrogen Bond* (Freeman, San Francisco, Cal., 1960).
- [48] W. HAGEN and A. G. G. M. TIELENS: *J. Chem. Phys.*, **75**, 4198 (1981).
- [49] M. VAN THIEL, E. D. BECKER and G. C. PIMENTEL: *J. Chem. Phys.*, **27**, 486 (1957).
- [50] G. J. JIANG, W. B. PERSON and K. G. BROWN: *J. Chem. Phys.*, **62**, 1201 (1975).
- [51] S. A. SANDFORD and L. J. ALLAMANDOLA: *Astrophys. J.*, in press, and references therein.
- [52] A. G. G. M. TIELENS, L. J. ALLAMANDOLA, J. BREGMAN, J. GOEBEL, L. B. D'HENDECOURT and F. C. WITTEBORN: *Astrophys. J.*, **287**, 697 (1984).
- [53] J. H. LACY, F. BAAS, L. J. ALLAMANDOLA, S. E. PERSSON, P. J. MCGREGOR, C. J. LONSDALE, T. R. GEBALLE and C. E. P. VAN DER BULT: *Astrophys. J.*, **276**, 533 (1984).
- [54] T. R. GEBALLE: *Astron. Astrophys.*, **162**, 248 (1986).
- [55] R. F. KNACKE and S. M. MCCORKLE: *Astron. J.*, **94**, 972 (1987).
- [56] Y. PENDLETON, A. G. G. M. TIELENS and M. W. WERNER: *Astrophys. J.*, **349**, 107 (1990).
- [57] R. F. KNACKE, S. M. MCCORKLE, R. C. PUETTER, E. F. ERICKSON and W. KRATSCHEMER: *Astrophys. J.*, **260**, 141 (1982).
- [58] K. M. MERRILL, R. W. RUSSELL and B. T. SOIFER: *Astrophys. J.*, **207**, 763 (1976).
- [59] W. HAGEN, A. G. G. M. TIELENS and J. M. GREENBERG: *Astron. Astrophys.*, **117**, 132 (1983).
- [60] R. GRIM, F. BAAS, W. SCHUTTE, J. M. GREENBERG and T. GEBALLE: *Astron. Astrophys.*, in press.
- [61] H. P. LARSON, D. S. DAVIS, J. H. BLACK and U. FINK: *Astrophys. J.*, **299**, 873 (1985).
- [62] R. J. A. GRIM and J. M. GREENBERG: *Astrophys. J. Lett.*, **321**, L91 (1987).
- [63] J. A. NUTH and M. H. MOORE: *Astrophys. J. Lett.*, **329**, L113 (1988).
- [64] A. G. G. M. TIELENS, A. TOKUNAGA, T. R. GEBALLE and F. BAAS: in preparation.
- [65] P. HOLLIM and J. PRITCHARD: in *Vibrational Spectroscopy for Adsorbed Species*, edited by A. T. BELL and M. L. HAIR (Academic Press, New York, N.Y., 1980), p. 51.
- [66] J. D. BREGMAN: in *Interstellar Dust*, edited by L. J. ALLAMANDOLA and A. G. G. M. TIELENS (Reidel, Dordrecht, 1989), p. 109.
- [67] R. J. A. GRIM: Ph. D. Thesis, Rijksuniversiteit Leiden (1988).